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TRANSITION-METAL CARBON CHEMISTRY

G. WILKINSON

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY
LONDON, ENGLAND

TECHNICAL REPORT ML-TDR-64-135

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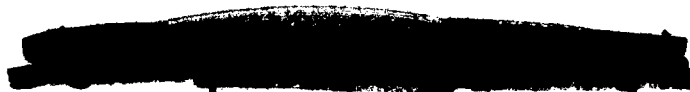
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FOREWORD

This report was prepared by the Imperial College of Science and Technology, London, England on USAF Grant No. AF EOAR 62-55 under Project 7342, "Fundamental Research on Macromolecular Materials and Lubrication Phenomena." Task 734201, "Basic Factors in the Synthesis of Macromolecular Materials." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Dr. Harold Rosenberg acting as project engineer.

This report covers work conducted from November 1962 to November 1963. The manuscript was released for publication as a Technical Report in March 1964.

The research reported in this document has been sponsored by the Research and Technology Division, AFSC, through the European Office of Aerospace Research, United States Air Force.

This technical report has been reviewed and is approved.

William E. Gibbs

WILLIAM E. GIBBS
Chief, Polymers Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

The use of hexafluorobut-2-yne for the preparation of inorganic complex compounds has been investigated. Compounds have been prepared which are complexes of tetrakis(trifluoromethyl)cyclopentadienone and hexakis(trifluoromethyl)benzene. They have been studied chemically and also structurally by X-ray diffraction.

SECTION I

PREPARATIVE STUDIES

Preparatory studies on transition-metal complexes derived from a perfluoroacetylene and metal carbonyls have been reported in Technical Note No. 1 (July 15, 1963). The important features of the work are:

(a) The preparation by the interaction of hexafluorobut-2-yne with carbon monoxide, using dicarbonylchlororhodium as catalyst, of the uncoordinated tetrakis(trifluoromethyl)cyclopentadienone. It was shown that this compound forms a variety of charge-transfer complexes with benzene and other organic solvents. It was also shown that this dienone reacts directly with metal carbonyls to give the cyclopentadienone derivatives previously

obtained by interaction, for example, of π -cyclopentadienyldicarbonylcobalt with hexafluorobut-2-yne.

(b) It was shown that the interaction of hexafluorobut-2-yne with π -cyclopentadienyldicarbonylrhodium gives rise not only to the tetrakis(trifluoromethyl)cyclopentadienone complex but also to a new complex, π -cyclopentadienylhexakis(trifluoromethyl)benzenerhodium. It was shown that the benzene ring is bound to the metal atom by two σ -bonds and a π -bond, to provide the first example of completely localized bonding of a benzene ring to a transitional metal.

SECTION II

STRUCTURAL STUDIES

Studies have been carried out on the X-ray determination of the molecular structure of these complexes, which has confirmed the main features discovered by nuclear magnetic resonance spectroscopy.

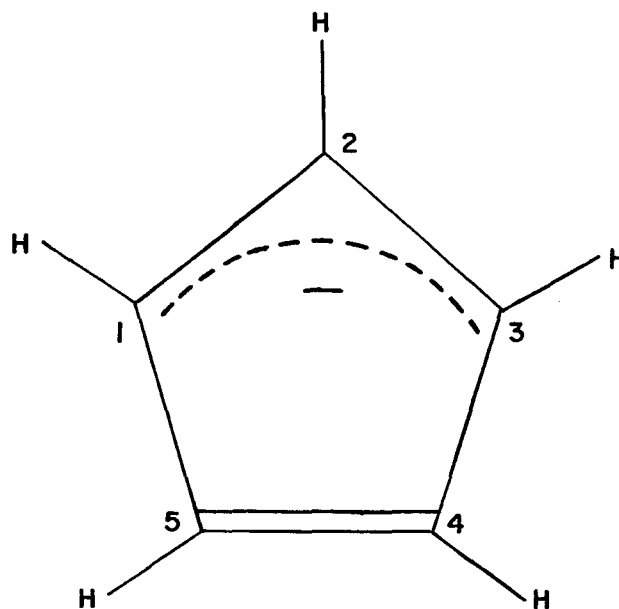
Perhaps the most significant results that have been obtained relate to the possibility of asymmetry in the bonding between a π -cyclopentadienyl ligand and a transition-metal ion. It is assumed, and generally accepted, that in the bis- π -cyclopentadienyls or any other π -cyclopentadienylmetal complex possessing essentially cylindrical symmetry around the metal ion (e.g. π -cyclopentadienylmanganese tricarbonyl) the carbon-carbon bond lengths in the cyclopentadienyl ring are all, within experimental error, identical. The molecular geometries summarized in Figure 1 are distinguished by (a) the lack of cylindrical symmetry around the metal ion and, we suggest, as a consequence (b) localization of electron density in the cyclopentadienyl ring; the standard deviations of the observed carbon-carbon bond lengths range from 0.02 to 0.03 Å so that significance can be attached to a number of the bond length differences of Figure 1.

In the cyclopentadienyl anion, the six π -electrons are distributed amongst the three molecular orbitals designated in the usual way as the a_1 , e_1^+ and e_1^- orbitals (Figure 2).

Provided the doubly degenerate e orbitals are equally occupied, there is uniformity of electron density around the ring and therefore identity of carbon-carbon bond lengths. Now a considerable proportion of the metal-ligand bonding arises from overlap of the degenerate d_{yz} and d_{xz} orbitals of the metal with the e molecular orbitals of the cyclopentadienyl ring. If the degeneracy of these metal orbitals were lifted through the field around the ion having less than cylindrical symmetry, there seems to be no a priori reason why the

respective molecular orbitals should combine equally with the e_1^+ and e_1^- molecular orbitals. In other words, the removal of metal orbital degeneracy also serves to remove the degeneracy of the bonding orbitals on the cyclopentadienyl ring.

If one formally writes the structure



as representing the bond lengths in the cyclopentadienyl ligand, one finds that the group of atoms C_1 , C_2 and C_3 is always trans to the relatively strong field ligands on the opposite side of the molecule, for example, the carbonyl groups and hydride ions. Thus, by either electrostatic effects, π -bonding or both, we obtain a perturbation of the 'd' orbitals which serves to remove their degeneracy over and above the normal crystal field-splitting effects. We thus obtain the situation that donation of electrons from the two degenerate e orbitals of the cyclopentadienyl ligand into metal 'd' orbitals is unequal with a concomitant loss of five-fold symmetry in the ligand.

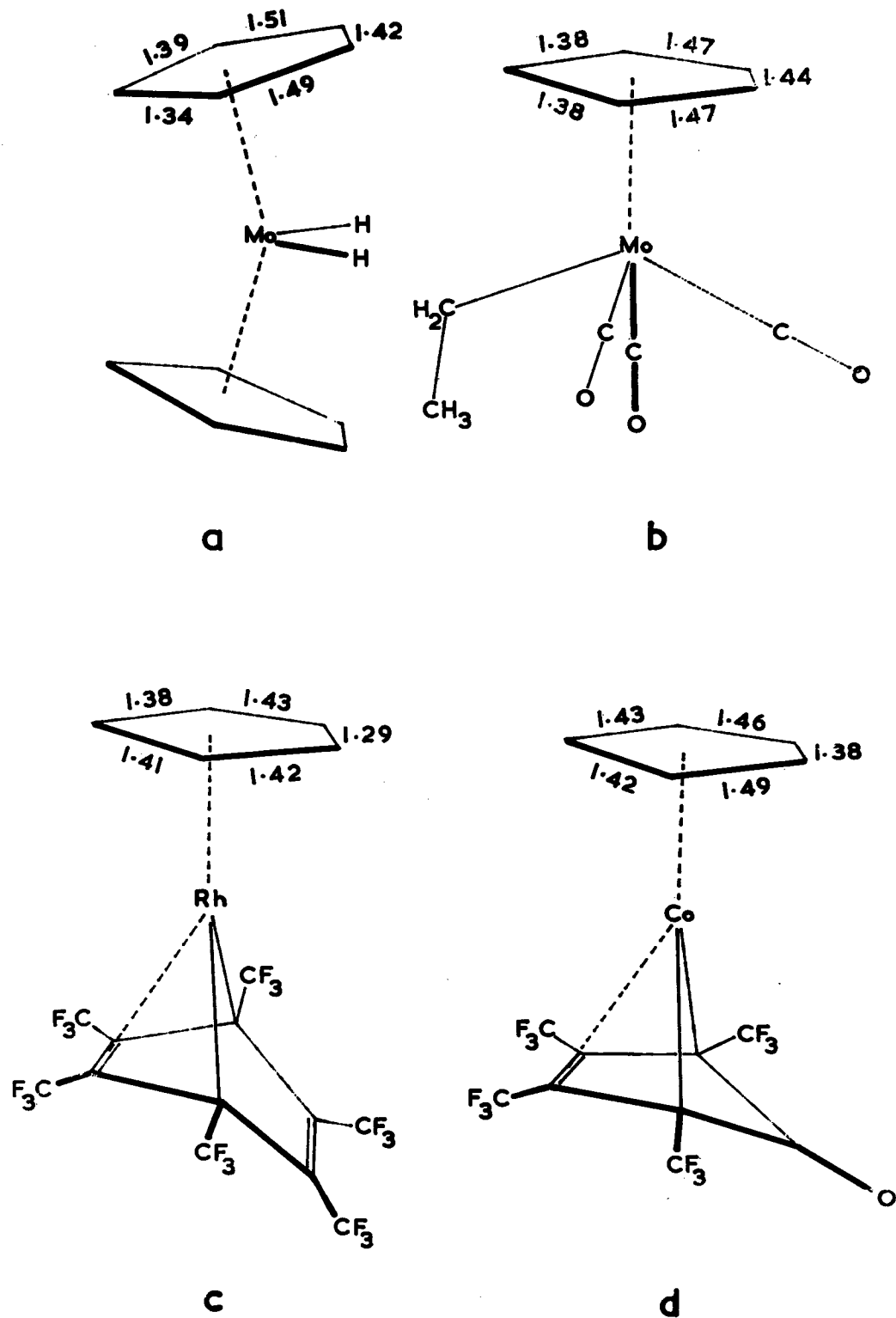
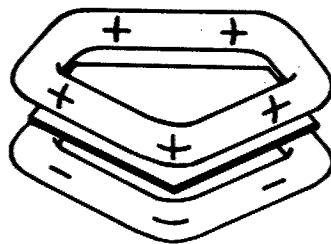
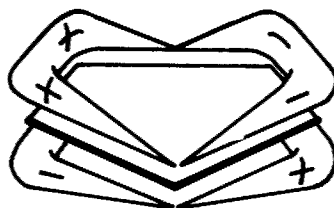


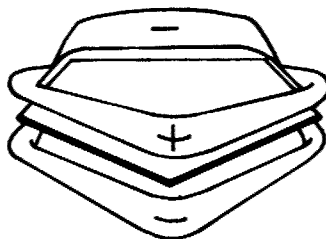
Figure 1



a



e_1^+



e_1^-

Figure 2

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